A

THESIS

ON

Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol

SUBMITTED FOR THE PARTIAL FULFILMENT OF

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BY

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2015

Department of Chemical Engineering
National Institute of Technology, Rourkela
CERTIFICATE

This is to certify that **Mr. Sabyasachi Mallick (Roll No. 213CH1120)** has carried out the project work titled "***Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol***" within the stipulated time. It is hereby approved that the work done by him is a creditable study in the field of chemical engineering and is carried out with all the details and precisions for the fulfilment of the purpose under my supervision and guidance.

Date: 25th May, 2015

Place: Rourkela

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ABSTRACT

The application of reactive extraction for the separation of butyric acid from its aqueous solution is a relatively new technique. It has many uses in different industries, and currently there is a great interest in using it as a precursor to biofuels. Research works are available on equilibrium study of the reactive extraction of butyric acid where aliquat-336 and tri-butyl phosphate were used as the reactive extractant. But no one has used TOA as the extractant, and nowhere study on the kinetic behaviour of reactive extraction of butyric acid has been done. Also the detailed study on the effect of temperature on the Butyric acid-TOA- Decanol system is unavailable. The present research work has focused on the reactive extraction of butyric acid from its aqueous solution using Tri-Octyl-Amine (TOA) in the active diluent decanol. Equilibrium and kinetic studies was performed at very low concentrations of butyric acid in water viz. 0.05M to 0.3M at 25^0C, 30^0C, 35^0C and 40^0C. The effect of temperature on the extraction equilibrium and kinetics was considered. In the equilibrium study, the complexation constant ($K_{E(1:1)}$) was evaluated and the type of complex formed was also determined. The distribution coefficient (K_D) and extraction efficiency (E%), were determined. In the kinetic study, the order of the reaction (n), the rate constant (k) and the mass transfer coefficient (K_L) were found from the experimental data. Extraction efficiency (E%) of 98% and distribution coefficient (K_D) of 49 has been achieved at 40^0C. The order of the reaction (n) has been found to be 1. The mass transfer coefficient (K_L) has been found to be 10.77×10^{-3} cm/min.

Keywords: Reactive extraction, butyric acid, decanol, equilibrium, kinetic study, TOA.

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NOMENCLATURE

Sl. No.	Notation	Definition
1	E%	Extraction efficiency in percentage (%)
2	$[HA]_{aq}$	Concentration of butyric acid in aqueous phase in gmol/lit
3	$[HA]_{org}$	Concentration of butyric acid in organic phase in gmol/lit
4	k	Rate Constant in $minute^{-1}$
5	K_D	Distribution coefficient
6	$K_{E(1:1)}$	Equilibrium complexation constant for 1:1 complex formation $in(gmol/lit)^{-1}$
7	K_L	Mass transfer coefficient in cm/min
8	v/v	Volume by volume basis.
9	Z	Loading Ratio

CHAPTER: 1
INTRODUCTION

1. Introduction

1.1. Background of the Present Research Work

The source of carboxylic acid is petroleum stock. But it is getting depleted day by day and with it the cost of the petroleum is also increasing. Alternately carboxylic acid can be obtained from bio-fermentation process. The quantity of the acid in the fermented product is very less, and it whips a challenging task to chemical engineers to recover the valuable carboxylic acid from the fermented product mixture. Many separation techniques are currently available for the recovery of the acid from aqueous solutions, including precipitation, distillation, solvent extraction, membrane process, and electro dialysis; however, most of these techniques are inappropriate as they consume large amounts of energy and chemicals and produce waste during the regeneration of separation agents. Recovery of these solute species can be achieved efficiently by reactive extraction.

Reactive extraction is a separation process which involves chemical reaction along with mass transfer. The extractant in the organic phase reacts with the acid in the aqueous phase and the reaction complexes formed are then solubilized in the organic phase. Extractants such as hydrocarbon, phosphorous, and aliphatic amine extractants are mainly used in the reactive extraction of carboxylic acids [1-11]. Reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as an efficient technique for the recovery of carboxylic acids.

1.2. Origin of the Work

Butyric acid is a short chain carboxylic acid that has many important applications in pharmaceutical, food, cosmetics and power industries. Because of its wide usage many researchers have focused on the reactive extraction of butyric acid from fermentation broth. Extractive separation of butyric acid from low concentration aqueous solutions by amine extractants has been found to be a promising technique. From thorough literature survey it was found that extraction of butyric acid using tri-octyl amine in decanol has not been studied previously. Hence, this work includes the equilibrium and kinetic studies of extraction of butyric acid using TOA as extractant and decanol as diluent.

1.3. Objectives

The main objectives of the research work are stated below:

I. Evaluation of the performance of equilibrium reactive extraction of butyric acid in terms of extraction efficiency (E%) and distribution coefficient (K_D) and using TOA as the extractant and decanol as solvent.

II. Finding out the effect of temperature on the performance of extraction equilibrium and kinetics.
III. Identification of the type of complex formed by butyric acid-TOA in organic phase, and finding the capacity of TOA in terms of loading ratio and complexation constant, K_E.
IV. Kinetic study of reactive extraction of butyric acid using TOA in decanol by evaluating rate constant, *k*, order of the reaction, *n* and mass transfer coefficient, K_L.

1.4. Thesis Summary

This thesis encompasses of five chapters *viz.* Introduction, Literature Review, Experiment, Results and Discussion and Conclusions. Each of these chapters adequately details about past and present research in similar fields, experimental methodologies followed, research findings and their possible explanations.

Chapter 1: Introduction of the field of research in brief, broad description of research background, objectives of this work and thesis overview.

Chapter 2: Discussion of the literature reports in detail pertaining to field of reactive extraction of carboxylic acids. Research works which are being carried out in the field of reactive extraction of carboxylic acids both nationally and internationally have been discussed. Various extractant-diluent systems for the recovery of carboxylic acids by reactive extraction have been introduced and elaborated.

Chapter 3: Description of the experimental methodologies including membrane preparation, concentration analysis, experimental procedure.

Chapter 4: Incorporates various results obtained during this study and their possible explanation of various observations is also given in detail.

Chapter 5: Summarization of the major highlights of this work and conclusion of the results and observation during this study.

Chapter 6: Enlightenment on the future work which could be carried out pertaining to the current project.

CHAPTER: 2
LITERATURE REVIEW

2. Literature Review

2.1. Reactive Extraction

The rapid industrialization and competitiveness have urged the chemical engineers to concentrate on units or processes whose waste generation and energy consumption are both low. Extraction process involves mass transfer with no heat transfer and hence found very much energy efficient.

Reactive extraction is a process intensification method coming under advanced separation techniques and is gaining great attraction particularly in terms of its comparison with the conventional extraction method, which have posed a great economic pressure to the industries carrying out them. The reactive extraction process has an important advantage of linking the two priorities of any chemical industry namely the conversion and selectivity. Here mass transfer is agglomerated with reaction leading to improved catalyst life, high local driving force for recovery leading to reduction of equipment sizes, elimination of recycle streams, reducing the by-product formation and reductions in utility costs.

The implementation of reactive extraction to the recovery of carboxylic acids has been found to be effective but the optimized process has to be determined for each carboxylic acid. The reactive extraction process involves the use of an extracting solvent to recover the targeted carboxylic acid whose efficiency is determined by the distribution coefficient (K_d). The distribution coefficient is defined as the ratio of the concentration of the acid in organic phase to the concentration of the acid in the aqueous phase. The concentration of the acid in the solution is determined by HPLC (High Performance Liquid Chromatography) system. The extractant reacts with the acid to form a complex which is separated against the other non-acidic components. A diluent is added to help in solvation of the extractants as they are sometimes found to be solid or viscous. The diluents help in improving the physical properties of the extractant. Most commonly used diluents include alcohols, ketones, esters, etc.

Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic acids. Reactive liquid-liquid extraction has the advantage that acid can be removed easily from the fermentation broth, preventing lowering of the pH. Further, acid can be re-extracted and the extractant recycled to the fermentation process. The advantages for reactive extraction with fermentation can be summarized as: Increased reactor productivity; Ease in reactor pH

control without use of base addition; Use of a high-concentration substrate as process feed to reduce process waste and production cost; produce and recover fermentation product in one continuous step and reduce downstream processing load and recovery cost.

2.2. Equilibrium Study

Butyric acid is a short chain carboxylic acid that has many important applications in various industries. It is a colourless liquid and has an unpleasant smell. It is soluble in water and many organic solvents. It has many uses in different industries, and currently there is a great interest in using it as a precursor to biofuels. It is a promising chemical that may hold the potential for future energy needs as it can be converted to butanol through biological transformation [12–14]. It is well known for its anticancer effects as it induces morphological and biochemical differentiation in a variety of cells leading to concomitant suppression of neoplastic properties. Butyric acid is used in the preparation of various butyrate esters. Low-molecular-weight esters of butyric acid, such as methyl butyrate, have mostly pleasant aromas or tastes. As a consequence, they find use as food and perfume additives. It is also used as an animal feed supplement, due to the ability to reduce pathogenic bacterial colonization. Because of its wide usage many researchers have focused on the reactive extraction of butyric acid from fermentation broth. Biosynthetic production of butyric acid for such purposes is preferred. In fermentative production of butyric acid, strong biosynthesis inhibition by the product occurs [15–17]. Possible solution of this problem lies in the separation of butyric acid from the fermentation solution by extraction. Extractive separations of butyric acid from low concentration solutions by classical solvents with reactive extractants, e.g. tri-alkyl amines, tri-butyl phosphate or others, diluted by hydrocarbons or alcohols have been widely studied by several authors [17–26].

However, tertiary amines offer advantages over other extractants because of their low cost, low solubility in water, good regenerability and high distribution coefficient, K_D. Tertiary amines were found effective in the extraction of lactic acid using alcohol as diluent. Using alcohol as diluent bestowed another advantage of formation of acidic ester which could be easily separated. [27]

A. Keshav, et al. have studied the reactive extraction of acrylic acid using Aliquat-336 as the extractant and Oleyl alcohol as the diluent. [26] The effects of temperature on the extractions of different monocarboxylic acids (acrylic, propionic, and butyric acids) were studied.

M.N. Ingale and V.V. Mahajani of have also studied the extraction of butyric acid from aqueous waste stream using Tri-butyl phosphate as extractant. [18-19] They have investigated the extraction process for single aqueous acid-extractant system and also aqueous acid mixture-extractant system and have studied the effect of presence of salts Na_2SO_4 and NaCl in the system. They found that the ease of extraction of the carboxylic acids in TBP in aqueous solution was of the order Caproic Acid>Valeric Acid>Butyric Acid. They also found that the K_D values were less in the presence of salts than in their absence for all acid concentration less than 2500 mg/lit. For acid concentration above 2500 mg/lit the presence of salt enhanced the K_D values. Higher K_D values were obtained for mixed system rather than individual aqueous acid system. Also the K_D values were higher for systems containing chloride ions than those containing sulphate ions.

J.A. Tamada and C.J.Kings [28] studied the effects of temperature on the extraction of succinic and lactic acids by Alamine 336 in methyl-isobutyl ketone (MIBK) and in chloroform. It was found that extraction decreases with increasing temperature. The apparent enthalpies of association were found to be more exothermic for succinic acid than for lactic acid and more exothermic in chloroform than in MIBK. The decrease in entropy of reaction was higher for succinic acid than for lactic acid and was greater in chloroform than in MIBK. For the systems studied, 1:1 acid-extractant complexation was found to be much more exothermic and to involve a much greater loss of entropy than the formation of 2:l or 3:l complexes.

Harington and Hossain [29] investigated the effect of temperature (283-313 K) on the extraction of lactic acid using 20% tri-n-octyl amine in sunflower oil at natural pH. Increasing the operating temperature increased the distribution coefficient (K_D). The trend was suggested to be a positive result because the optimal temperature of fermentation broths is around 38°C. Therefore, performing the extraction around this temperature would allow greater extraction than at room temperature.

For the equilibrium study on reactive extraction many researchers have performed several investigations. Y.K. Hong, et al. [1] have studied the application of reactive extraction to the recovery of carboxylic acids and have categorized three different kinds of extractants namely carbon-bonded oxygen-bearing extractants, phosphorous-bonded oxygen-bearing extractants and proton transfer or ion-pairing formation with high molecular weight aliphatic amines and

their salts. The works also identifies the various diluents to be used for the process and the amine based extraction of citric acid is discussed. The technique of solvent regeneration and stripping of extracted acid is studied.

S.T. Yang, et al, [30] have researched on the extraction of lactic, butyric, propionic and butyric acid with tertiary and quaternary amines and the effect of pH on the process and have studied the application of the principle of mass action law modelling to interpret the results of reactive extraction of butyric, lactic, succinic, malonic, fumaric, and maleic acids by Alamine 336, an aliphatic, tertiary amine extractant, dissolved in various diluents. The results of mass action law modelling have been combined with the spectroscopic results to analyse the chemical interactions involved in carboxylic acid complex formation with amine extractants. Co-extraction of water during extraction of succinic acid by Alamine 336 in various diluents has been studied.

X. Shan, et al, [25] have researched on the extraction from aqueous solution experiments, using five types of mixed solvents and 12 monocarboxylic acids. From the results of these experiments, a new mathematical model, including a new definition of extractant's basicity (pKa, BS), was developed and validated. Trioctylamine (TOA)/1-octanol, TOA/methyl iso-butyl ketone (MIBK), TOA/tetrachloromethane (CCl4), trialkylphosphine oxide (TRPO) /1-octanol and TRPO/ kerosene, were used as the extractant, and formic, butyric, propionic, valeric, caproic, cholorobutyric, dichlorobutyric, trichlorobutyric, glycolic, glyoxylic, and lactic acids, were used as the solutes extracted.

2.3. Kinetic Study

The kinetic study of reactive extraction has been investigated by many researchers. K.L. Wasewar, et al, [27] studied the reactive extraction of lactic acid using Alamine-336 in n-decanol has been studied. The equilibrium complexation constants for ratios of (1:1) and (2:1) have been estimated. The kinetics of extraction of lactic acid by Alamine 336 in decanol has also been determined. A. Keshav, et al,[26] investigated the reactive extraction of acrylic, propionic and butyric acid using Aliquat 336 in oleyl alcohol was carried out and the effect of temperature was studied from 305-333K. The effect of temperature on the partition coefficient was evaluated. The enthalpy and entropy of the reaction were evaluated at different temperatures.

The model of an amine extraction process requires equilibrium and kinetic data of the acid-extractant - diluent system employed. The effect of temperature is an important matter of

investigation in the reactive extraction processes in view of operating temperatures and back-extraction/regeneration steps. In this field, few research works are available for equilibrium study and very little information are available on kinetic study of the process. Also detailed study on the effect of temperature on the particular acid-extractant- diluent system is not available. From the literature survey, we can get knowledge that kinetic studies of reactive extraction of butyric acid using amine extractant namely TOA in active diluent decanol in first front have not been investigated and also the effect of temperature on this particular extractant system should also be studied.

CHAPTER: 3

MATERIALS AND METHODS

3. Materials and Methods

3.1. Materials

Butyric acid (Merck Specialist) and decanol (Loba Chemie) used were of reagent grade. Tri-octyl Amine (Otto, 99%, Density-0.816 g/ml, Solubility in water 0.2g/lit) used was of analytical grade. The aqueous solutions were prepared using distilled water. The initial concentration of butyric acid was varied from 0.05 gmol/lit. to 0.3 gmol/lit.[31] as in the practical case the concentration of butyric acid in fermentation broth is very low and varies within the mentioned range. Sodium hydroxide (NaOH) used for titration was of laboratory grade. For the standardization of the NaOH, oxalic acid (mass fraction of 99.8%) was used. Phenolphthalein solution (pH range 8.2 to 10.0) was used as an indicator. The TOA concentration in decanol was varied from 0% to 10% on volume by volume basis. The aqueous phase consisted of butyric acid dissolved in water and the organic phase consisted of TOA dissolved in decanol.

The chemicals used in conducting the experiments are given below:

Table 3.1: **List of Chemicals used in the present work**

Sl. No.	**Name of the Chemical**	**Manufacturing Company**	**Properties at 25^0C**
1	Butyric Acid	Otto	Density: 959.5kg/m^3, soluble in water
2	Decanol	Otto	Density 829.7 kg/m^3, Insoluble in water:
3	Tri-Octyl Amine (95%)	Otto	Density-0.816 g/ml, solubility in water 0.2g/lit
4	NaOH Pellets	Fisher Scientific	Assay-98%
5	Oxalic Acid Pellets	Fisher Scientific	Assay-99%
6	Acetone	RFCL Ltd.	Density-0.781-0.791gm/ml.
7	Phenolphthalein	RFCL Ltd.	pH range- 8.2 to 10

3.2. Methods

3.2.1. Equilibrium Study

The experimental method included the following steps:

1. **Preparation of aqueous phase solution:** The aqueous butyric acid solution of desired concentration (<1M) was prepared in a 100ml. conical flask by dissolving butyric acid in water and stirring it well for uniform mixing.
2. **Preparation of organic phase solution:** The organic phase solution was prepared by dissolving the extractant in the diluent in different volume by volume ratio in a 100ml. conical flask. Here, tri-octyl amine is used as extractant and decanol is used as diluent.
3. **Mixing of aqueous phase and organic phase solutions:** The two phases were taken in equal volume of 10 ml. in a 100ml. conical flask was mixed in a water bath shaker or an incubator shaker for 8 hours. The temperature of the shaker was set at 25^{o}C, 30^{o}C, 35^{o}C and 40^{o}C. The speed of the incubator shaker is fixed at 120 rpm.
4. **Settling of the mixture:** After mixing when the equilibrium was achieved the solution was allowed to settle for 10 minutes so the organic phase and the aqueous phase settled separately over one another. Here organic phase being lighter in density settled above aqueous phase.
5. **Separation of aqueous phase:** After the mixture had settled the aqueous phase was selectively separated from the mixture by using a separating funnel.
6. **Evaluation of acid content in aqueous phase:** The acid present in the aqueous phase after extraction was evaluated by the method of titration wherein standardized NaOH solution was used. NaOH solution was standardized by using Oxalic acid solution of same concentration. Here, phenolphthalein was used as indicator. The end point of the titration process was indicated by the light pink colour aqueous phase solution. The titration was repeated three times for the same sample and average reading was taken for estimating butyric acid. Normality is defined as number of gram equivalents of the solute present in 1000 ml solution. If W g of solute of equivalent weight E is present in V mL of the solution, the normality of the solution is given by:

$$\text{Normality} = \frac{W \times 100}{E \times V} \qquad 3.1$$

In the neutral solution,

$$N_1V_1=N_2V_2 \quad (3.2)$$

Where,

N_1 normality of titrant, aqueous solution of butyric acid

N_2 normality of titrate, caustic solution

V_1 volume of titrant, aqueous solution of butyric acid

V_2 volume of titrate, caustic solution

N_1 is calculated for the know values of V_1, N_2 and V_2.

7. **Evaluation of acid content in organic phase:** The acid content in the aqueous phase was evaluated by mass balance relation. Since the aqueous phase was very dilute and the chances of mixing of solvent with the acid were present, UV Spectroscopy analysis of the organic phase was carried out.
8. **Determination of distribution coefficient (K_D) :** The K_D value was evaluated using the formula-

$$K_D = \frac{[A]org}{[A]aq} \quad (3.3)$$

Where, $[A]_{org}$= Concentration of acid in organic phase.

$[A]_{aq}$= Concentration of acid in aqueous phase.

9. **Determination of extraction efficiency (E%):** The extraction efficiency of tri-octyl amine (TOA) was determined by the following formula-

$$E\% = \frac{\text{Concentration of acid in organic phase after extraction}}{\text{Concentration of acid before extraction}} \quad (3.4)$$

10. **Determination of loading ratio (Z):** The extent to which organic phase (TOA+Decanol) can be loaded with carboxylic acid is expressed as the loading ratio, Z;

$$Z = \frac{[HA]org}{[B]i,org} \quad (3.5)$$

Where, $[HA]_{org}$= Concentration of acid in organic phase after extraction.

$[B]_{org}$= Concentration of TOA in organic phase before extraction.

For very low loading ratios ($z<0.5$) the (1:1) complex is formed and the following equation holds;

$$\frac{Z}{(1-Z)} = K_{E(1:1)} * [HA]_{aq} \quad (3.6)$$

For higher loading ratios, the (2:1) complex is formed and the following equation holds;

$$\frac{Z}{(2-Z)} = K_{E(2:1)} * [HA]^2_{aq} \quad 3.7$$

The values of $K_{E(1;1)}$ and $K_{E(2:1)}$ are determined by plotting the graph of z/(1-z) versus $[HA]_{aq}$ or z/(2-z) versus $[HA]^2_{aq}$.

K_E= equilibrium complexation constant for the reaction between aqueous phase acid and organic phase extractant.

3.2.2. Kinetic Study

The experimental method includes the following steps:

1. **Preparation of aqueous phase solution:** The aqueous butyric acid solution of desired concentration (<1M) was prepared in a 250 ml. conical flask by dissolving butyric acid in water and stirring it well for uniform mixing.
2. **Preparation of organic phase solution:** The organic phase solution was prepared by dissolving the extractant in the diluent in different volume by volume ratio in a 100ml. conical flask. There, tri-octyl amine was used as extractant and decanol was used as diluent.
3. **Mixing of aqueous phase and organic phase solutions:** The two phases were taken in equal volume of 100 ml. in a 250 ml. conical flask is mixed in a digital magnetic stirrer cum heater. The experiment was conducted for about 5 hours. The temperature of the stirrer cum heater was set at 25^{o}C, 30^{o}C, 35^{o}C and 40^{o}C. The speed of the stirrer was set at 180 rpm.
4. **Taking out samples at equal time intervals:** The sample from the reaction mixture was taken out using a 10 ml pipette at equal time interval of 30 minutes.
5. **Evaluation of acid content in aqueous phase:** The acid present in the aqueous phase after extraction was evaluated by the method of titration wherein standardized NaOH solution was used. NaOH solution was standardized by using Oxalic acid solution of same concentration. Here, phenolphthalein was used as indicator. The end point of the titration process was indicated by the light pink colour aqueous phase solution. The titration was repeated three times for the same sample and average reading was taken

for estimating butyric acid. Normality is defined as number of gram equivalents of the solute present in 1000 ml solution. If W g of solute of equivalent weight E is present in V mL of the solution, the normality of the solution is given by equation-(3.1):

$$\text{Normality} = \frac{W \times 100}{E \times V}$$

In the neutral solution, the equation-(3.2) gives:

$$N_1V_1 = N_2V_2$$

Where,

N_1 normality of titrant, aqueous solution of butyric acid

N_2 normality of titrate, caustic solution

V_1 volume of titrant, aqueous solution of butyric acid

V_2 volume of titrate, caustic solution

N_1 is calculated for the know values of V_1, N_2 and V_2.

6. **Evaluation of acid content in organic phase:** The acid content in the aqueous phase was evaluated by mass balance relation. Since the aqueous phase was very dilute and here chances of mixing of solvent with the acid were present, UV Spectroscopy analysis of the organic phase was carried out.
7. **Determination of the mass transfer coefficient (K_L):** The value of mass transfer coefficient can be obtained from the following equation-

$$V_{aq} \times \frac{dC_{org}}{dt} = K_L \times A_C \times (C^*_{org} - C_{org}) \qquad 3.8$$

On integrating equation-(8), we get.

$$K_L = \frac{V_{aq}}{A_c \times t} \int \frac{dC_{org}}{\left(C^*_{org} - C_{org}\right)} \qquad 3.9$$

Where,

V_{aq}= Volume of aqueous phase.

A_c= Cross-Sectional area of base of conical flask.

t = Time of extraction.

C_{org}= Concentration of butyric acid in organic phase.

C^*_{org}= Equilibrium concentration of butyric acid in organic phase.

The mass transfer coefficient was obtained by evaluating equation-(3.9)

8. **Determination of the order of the reaction (n):** The order of the reaction was determined by integral method of analysis of the kinetics data available from the experiments.

9. **Determination of the reaction rate constant (k):** The reaction rate constant was determined from the rate expression by means of curve fitting.

Each of the experiment was carried out three times to check the consistency and it was found to be within the reasonable limit of ±2%.

3.2.3. Analytical Instrument

For measuring concentration of different phases, UV-Visible spectroscopy method was used (JASCO V-750 model). pH measurements of aqueous phases were carried out by pH meter (Hanna, USA).

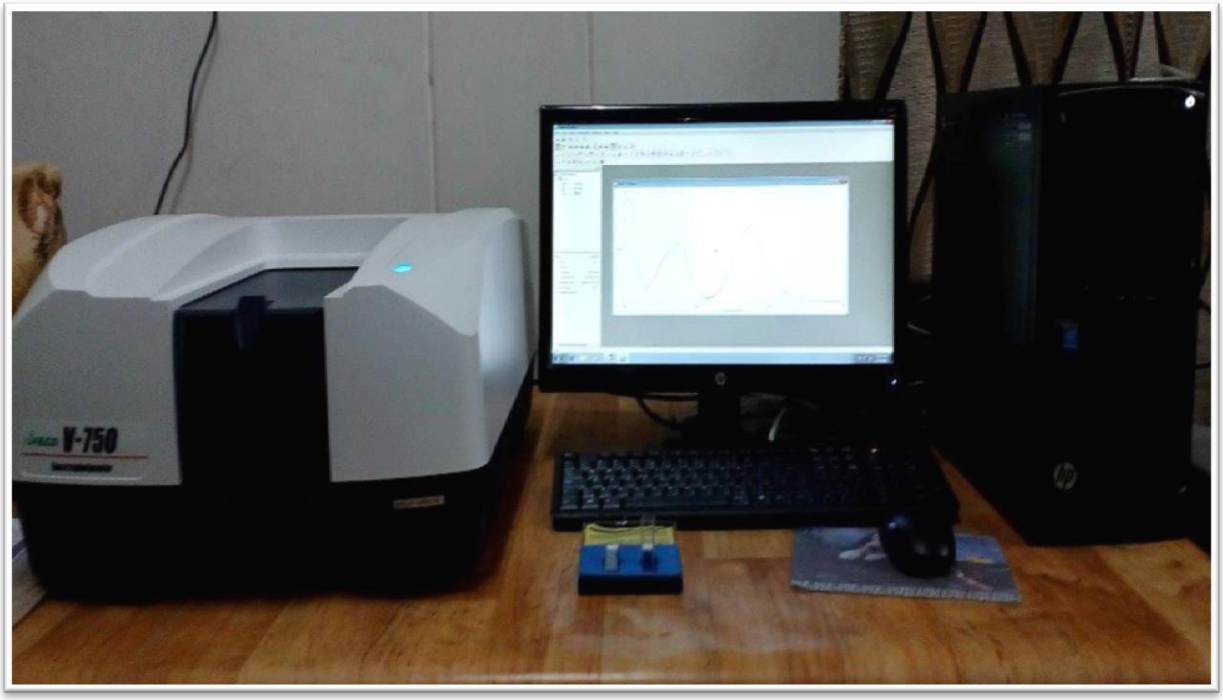

Figure: 3.1- UV-Visible spectrophotometer with attached desktop

For measuring concentration of different phases, UV-Visible spectroscopy method was used (JASCO V-750 model). Samples (5ml) from the each organic phase were taken periodically from and analysed using UV-Visible spectroscopy. UV-Visible spectroscopy is one of the simplest instruments for determined Cr (VI) concentration. Uses of coupled plasma (ICP-OES and ICP-MS) spectrometry and atomic absorption spectrophotometry (AA) are also reported for determining chromate ion concentration.

The concentration is measured with UV-Vis spectroscopy using the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is-

$$A = \log (I_0/I) = \varepsilon \times c \times l \qquad 3.10$$

Where, A = Absorbance

I_0 = Intensity of light incident upon sample cell

I = Intensity of light leaving sample cell

C = Molar concentration of solute

L = Length of sample cell (cm.)

Ɛ= Molar absorptivity

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

Firstly calibration curve is established with known concentrations, 0.1M, 0.2M, 0.3M, 0.4M and 0.5M butyric acid in decanol. The calibration curves obtained of determination of acid content in the organic phase can be seen in Figure: 3.1.

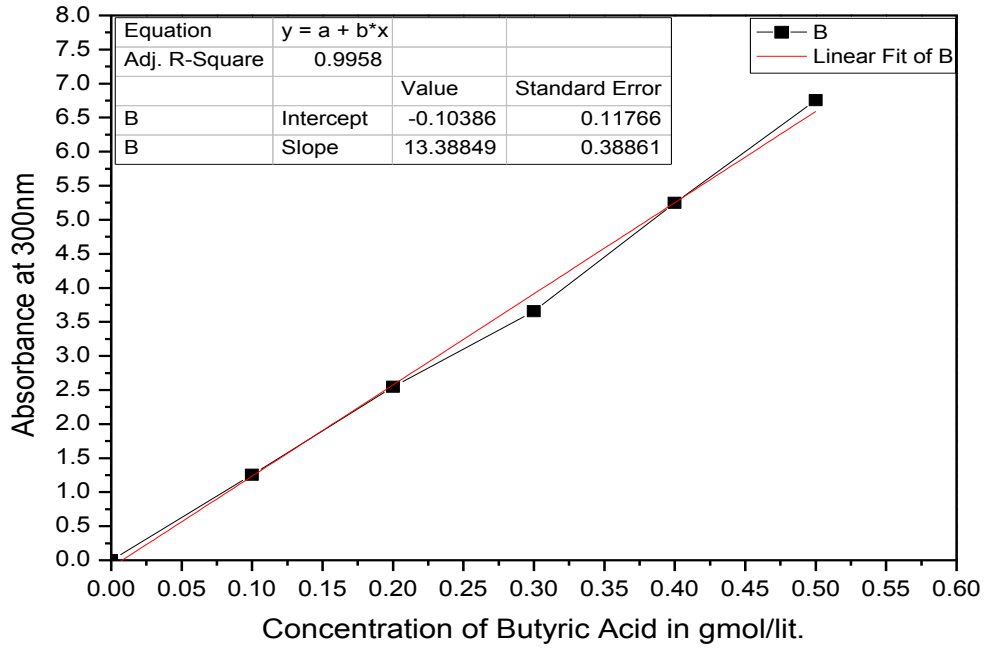

Figure: 3.2- Calibration curve for the evaluation of butyric acid content in the organic phase

Concentration of samples was found by comparing its UV absorbance with standard curve.

3.2.4. Experimental Instrument

Digital magnetic stirrer cum heater (LABMAN Scientific Instruments) was used to conduct the kinetics experiments. It can operate up to 500 ml of stirring volume and a temperature range 0-400^{0}C. A probe is provided to record the temperature of the stirring volume. A 250 ml conical flask was used as the batch reactor. The experiment was conducted for 5 hours and samples were taken out regular intervals of 30 minutes.

Figure: 3.3- Conical flask kept over digital magnetic stirrer cum heater with reaction mixture

Fig: 3.4- Sample tubes containing the samples taken out periodically with distinct organic phase and aqueous phase

CHAPTER: 4
RESULTS AND DISCUSSIONS

4. Results & Discussions

4.1. Extraction Equilibria

The mechanism of the reactive extraction of butyric acid, HA, with TOA was verified by taking into consideration the following expressions of the interfacial reaction between solute and extractant:

$$[R_3N]_{(org)} + [HA]_{(aq)} \rightleftharpoons [R_3NH^+A^-]_{(org)} \quad 4.1$$

In the amine-based extraction of carboxylic acid, the reaction between carboxylic acid and amine can be described in various ways. Equilibrium data of amine-based extraction can be explained by the mass action law based on the following reactions. [32]

Some assumptions in the present description are required as follows:

(1) The solubility of TOA in the aqueous phase is negligible.

(2) TOA reacts only with the undissociated form of acid.

It was known that carboxylic acids could exist as dimers in the organic phase because of the intermolecular hydrogen bonding. [30] Based on these assumptions, the reactions of monocarboxylic acid by TOA can be described as follows:

$$HA + R_3N \leftrightarrow HA–R_3N \quad 4.2$$

$$2HA + R_3N \leftrightarrow (HA)_2– R_3N \quad 4.3$$

Experiments for the extraction of butyric acid with TOA in decanol was carried out at four different temperatures viz. 25^0C, 30^0C, 35^0C and 40^0C. Four different initial concentrations of 0.05M, 0.1M, 0.15M and 0.2M aqueous butyric acid solution was taken. At first physical extraction was carried out for each combination of experiment, then chemical extraction was carried out with two different concentrations of TOA in decanol viz. 5% and 10% on volume by volume basis. Each experiment was carried out three times to check the data consistency and it was found to be within the reasonable limit of $\pm 2\%$.

The results of the physical and chemical extraction are tabulated in the next page. The equilibrium complexation constant ($K_{E(1:1)}$) is expressed in $(\text{gmol/lit.})^{-1}$.

Table: 4.1-Extraction of 0.05M butyric acid using TOA in decanol at 25^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.0200	0.0300	0	0	0	0	0.67	40
5	0.0400	0.0100	53.82	0.35	0.54	0.21	4.00	80
10	0.0425	0.0075	30.43	0.19	0.23	0.10	5.67	85

Table: 4.2-Extraction of 0.05M butyric acid using TOA in decanol at 30^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.0200	0.0300	0	0	0	0	0.67	40
5	0.0420	0.0080	72.59	0.37	0.58	0.22	5.25	84
10	0.0445	0.0055	43.91	0.19	0.24	0.11	8.09	89

Table: 4.3-Extraction of 0.05M butyric acid using TOA in decanol at 35^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.0210	0.0290	0	0	0	0	0.72	42
5	0.0435	0.0065	94.54	0.38	0.61	0.23	6.69	87
10	0.0465	0.0035	72.91	0.20	0.25	0.11	13.28	93

Table: 4.4-Extraction of 0.05M butyric acid using TOA in decanol at 40^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.0220	0.0280	0	0	0	0	0.78	44
5	0.0445	0.0055	115.89	0.39	0.64	0.24	8.09	89
10	0.0475	0.0025	104.84	0.21	0.26	0.11	19.00	95

From the tables: 4.1.1- 4.1.4, it can be observed that for the physical extraction of 0.05M butyric acid at four different temperatures, the extraction efficiency increased from 40% to 44% and distribution coefficient increased from 0.67 to 0.78. The increase in distribution coefficient and extraction efficiency can be attributed to the active nature of decanol. The activity of the solvent increased with rise in temperature. The chemical extraction of 0.05M butyric acid at four different temperatures, showed better result than the physical extraction. The distribution coefficient increased from 4 to 8.09 for extraction using 5% TOA (v/v) and from 5.67 to 19 for 10% TOA (v/v). Similarly the extraction efficiency also increased from 80 to 89% for 5% TOA (v/v) and from 85 to 95% for 10% TOA (v/v). The increase in distribution coefficient and extraction efficiency with rise in temperature can be explained by the rise in solvation power of decanol which enables greater acid-amine complex formation.

Table: 4.5-Extraction of 0.1M butyric acid using TOA in decanol at 25^0C

Percentage of TOA used in %	**$[HA]_{org}$ in gmol/lit**	**$[HA]_{aq}$ in gmol/lit**	**Complexation constant, $K_{E(1:1)}$**	**Loading ratio (z)**	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	**Distribution coefficient K_D**	**Extraction Efficiency (E%)**
0	0.035	0.065	0	0	0	0	0.54	35
5	0.082	0.018	31.04	0.36	0.56	0.22	4.56	82
10	0.088	0.012	19.85	0.19	0.24	0.11	7.33	88

Table: 4.6-Extraction of 0.1M butyric acid using TOA in decanol at 30^0C

Percentage of TOA used in %	**$[HA]_{org}$ in gmol/lit**	**$[HA]_{aq}$ in gmol/lit**	**Complexation constant, $K_{E(1:1)}$**	**Loading ratio (z)**	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	**Distribution coefficient K_D**	**Extraction Efficiency (E%)**
0	0.039	0.061	0	0	0	0	0.64	39
5	0.084	0.016	36.28	0.37	0.58	0.22	5.25	84
10	0.090	0.010	24.56	0.19	0.24	0.11	9.00	90

Table: 4.7-Extraction of 0.1M butyric acid using TOA in decanol at 35^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.042	0.058	0	0	0	0	0.72	42
5	0.088	0.012	52.12	0.39	0.6255	0.24	7.33	88
10	0.092	0.008	31.46	0.20	0.2517	0.11	11.5	92

Table: 4.8-Extraction of 0.1M butyric acid using TOA in decanol at 40^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.045	0.055	0	0	0	0	0.82	45
5	0.091	0.009	73.42	0.39	0.66	0.25	10.11	91
10	0.095	0.005	52.42	0.21	0.26	0.12	19.00	95

From the tables: 4.1.5- 4.1.8, it can be observed that for the physical extraction of 0.1M butyric acid at four different temperatures, the extraction efficiency increased from 35% to 45% and distribution coefficient increased from 0.54 to 0.82. The increase in distribution coefficient and extraction efficiency can be attributed to the active nature of decanol. The activity of the solvent increased with rise in temperature. The chemical extraction of 0.1M butyric acid at four different temperatures, yielded better result than the physical extraction. The distribution coefficient increases from 4.56 to 10.11 for extraction using 5% TOA (v/v) and from 7.33 to 19 for 10% TOA (v/v). Similarly the extraction efficiency also increased from 82 to 91% for 5% TOA (v/v) and from 88 to 95% for 10% TOA (v/v). The increase in distribution coefficient and extraction efficiency with rise in temperature can be explained by the rise in solvation power of decanol which enables greater acid-amine complex formation.

Table: 4.9-Extraction of 0.15M butyric acid using TOA in decanol at 25^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.055	0.095	0	0	0	0	0.58	36.67
5	0.125	0.025	22.93	0.36	0.57	0.22	5.00	83.33
10	0.135	0.015	16.34	0.20	0.24	0.11	9.00	90

Table: 4.10-Extraction of 0.15M butyric acid using TOA in decanol at 30^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.059	0.091	0	0	0	0	0.65	39.33
5	0.130	0.020	30.51	0.38	0.61	0.23	6.50	86.67
10	0.140	0.010	25.64	0.20	0.25	0.11	14.0	93.33

Table: 4.11-Extraction of 0.15M butyric acid using TOA in decanol at 35^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.062	0.088	0	0	0	0	0.70	41.33
5	0.135	0.015	43.27	0.39	0.65	0.24	9.00	90.00
10	0.144	0.006	44.27	0.21	0.26	0.12	24.0	96.00

Table: 4.12-Extraction of 0.15M butyric acid using TOA in decanol at 40^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.068	0.082	0	0	0	0	0.83	41.33
5	0.140	0.010	68.97	0.41	0.69	0.25	14.0	93.33
10	0.146	0.004	67.57	0.21	0.27	0.12	36.5	97.33

From the tables: 4.1.9- 4.1.12, it can be observed that for the physical extraction of 0.15M butyric acid at four different temperatures, the extraction efficiency increased from 36.67% to 41.33% and distribution coefficient increased from 0.58 to 0.83. The increase in distribution coefficient and extraction efficiency can be attributed to the active nature of decanol. The activity of the solvent increased with the rise in temperature. The chemical extraction of 0.15M butyric acid at four different temperatures, yielded better result than the physical extraction. The distribution coefficient increased from 5 to 14 for extraction using 5% TOA (v/v) and from 9 to 19 for 10% TOA (v/v). Similarly the extraction efficiency also increased from 83.33 to 93.33% for 5% TOA (v/v) and from 90 to 97.33% for 10% TOA (v/v). The increase in distribution coefficient and extraction efficiency with rise in temperature can be explained by the rise in solvation power of decanol which enables greater acid-amine complex formation.

Table: 4.13-Extraction of 0.2M butyric acid using TOA in decanol at 25^0C

Percentage of TOA used in %	**$[HA]_{org}$ in gmol/lit**	**$[HA]_{aq}$ in gmol/lit**	**Complexation constant, $K_{E(1:1)}$**	**Loading ratio (z)**	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	**Distribution coefficient K_D**	**Extraction Efficiency (E%)**
0	0.080	0.120	0	0	0	0	0.67	40
5	0.170	0.030	19.73	0.37	0.59	0.22	5.67	85
10	0.184	0.016	15.74	0.20	0.25	0.11	11.5	92

Table: 4.14-Extraction of 0.2M butyric acid using TOA in decanol at 30^0C

Percentage of TOA used in %	**$[HA]_{org}$ in gmol/lit**	**$[HA]_{aq}$ in gmol/lit**	**Complexation constant, $K_{E(1:1)}$**	**Loading ratio (z)**	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	**Distribution coefficient K_D**	**Extraction Efficiency (E%)**
0	0.085	0.115	0	0	0	0	0.740	42.5
5	0.178	0.022	28.98	0.39	0.64	0.24	8.090	89.0
10	0.188	0.012	21.57	0.21	0.26	0.11	15.67	94.0

Table: 4.15-Extraction of 0.2M butyric acid using TOA in decanol at 35^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.088	0.112	0	0	0	0	0.790	44.0
5	0.183	0.017	39.26	0.40	0.67	0.25	10.76	91.5
10	0.194	0.006	44.90	0.21	0.27	0.12	32.33	97.0

Table: 4.16-Extraction of 0.2M butyric acid using TOA in decanol at 40^0C

Percentage of TOA used in %	$[HA]_{org}$ in gmol/lit	$[HA]_{aq}$ in gmol/lit	Complexation constant, $K_{E(1:1)}$	Loading ratio (z)	$\frac{z}{(1-z)}$	$\frac{z}{(2-z)}$	Distribution coefficient K_D	Extraction Efficiency (E%)
0	0.091	0.109	0	0	0	0	0.830	45.5
5	0.188	0.012	58.2	0.41	0.69	0.26	15.67	94.0
10	0.196	0.004	68.2	0.21	0.27	0.12	49.00	98.0

From the tables: 4.1.13- 4.1.16, it can be observed that for the physical extraction of 0.2M butyric acid at four different temperatures, the extraction efficiency increased from 36.67% to 41.33% and distribution coefficient increased from 0.58 to 0.83. The increase in distribution coefficient and extraction efficiency can be attributed to the active nature of decanol. The activity of the solvent increased with rise in temperature. The chemical extraction of 0.2M butyric acid at four different temperatures, showed better result than the physical extraction. The distribution coefficient increased from 5.67 to 15.67 for extraction using 5% TOA (v/v) and from 11.5 to 49 for 10% TOA (v/v). Similarly the extraction efficiency also increased from 85 to 94% for 5% TOA (v/v) and from 92 to 98% for 10% TOA (v/v). The increase in distribution coefficient and extraction efficiency with rise in temperature can be explained by the rise in solvation power of decanol which enables greater acid-amine complex formation.

From the tables, it is clearly observed that both the extraction efficiency and distribution coefficient increases significantly from physical extraction to chemical extraction. For higher extractant concentration high value of extraction efficiency of 98% is achieved at 40^0C. Also distribution coefficient of very high value of 49 is achieved at 40^0C.

For the physical extraction of butyric acid using decanol only, highest extraction efficiency of 45.5% was achieved at 40^0C for the extraction of 0.2M aqueous butyric acid solution. Also the highest distribution coefficient value of 0.83 was obtained for the same butyric acid concentration of 0.2M.

The reason behind the low distribution coefficient and extraction efficiency can be traced back to the fact that decanol is a higher alcohol with a negative ion donating functional group (OH^-). The acid molecules react with the alcohol and are not available as free acid in the organic phase. Since, decanol is a higher alcohol and the reaction between alcohol and carboxylic acid of higher order is not favoured due to the steric hindrance caused by the long aliphatic hydrocarbon chain that trails behind the reacting species. Due to the low solubility of butyric acid in organic solvents immiscible with water, its separation by physical extraction is not efficient. Although very low but distribution coefficient and extraction efficiency increased with temperature. This can be attributed to the active nature of decanol which is a highly polar solvent. The increase of temperature increased the activity of decanol and hence increase in extraction of butyric acid was observed.

The chemical extraction of butyric acid with TOA in decanol yielded satisfactory result. The distribution coefficients and extraction efficiencies were evaluated for different concentrations of TOA in decanol and at different temperatures. Starting with 4 for extraction of 0.05M butyric acid solution using 5% TOA in decanol at 25^0C, the distribution coefficient values have significantly increased up to 49 for 0.3M butyric acid solution using 10% TOA in decanol at 40^0C. Also, the extraction efficiency has improved from 80% for extraction of 0.05M butyric acid solution using 5% TOA in decanol at 25^0C, to 98% for 0.3M butyric acid solution using 10% TOA in decanol at 40^0C. In general, the diluents control the viscosity, density, and interfacial tension of the mixed solvent. The diluents used in the process also have an influence on the stoichiometry of the acid-amine complexes, the loading of the amine, as well as the third phase formation. The use of active diluent, decanol has also played an important role in the improvement of the distribution coefficient and extraction efficiency. Active diluents have functional groups that enable a greater solvation of the acid-amine complex. The solvent polarity controls the structure of the interfacial compounds formed by reaction between butyric acid and TOA. The reactive extraction of monocarboxylic acids with an amine occurs by means of the interfacial interactions between the solute and the extractant. These interactions could be of hydrogen bonding type, for the undissociated acid, or of ionic type, if the acid dissociates in the aqueous solution. The extraction efficiency and distribution

coefficient depend upon the association ability between butyric acid and TOA and the steric effect between the acid and the extractant. The diluent decanol increases the organic phase polarity and, consequently, exhibits a favourable effect on the solubilisation of polar molecules. Moreover, it possesses the ability to induce the breakage of the stable "third phase" emulsion which appears in the system because of using TOA as extractant, being called "phase modifier". The high values of distribution coefficient and extraction efficiency result from the formation of solvates through specific ionic pair bonding between the proton of the diluent and the electron of the acid−amine complex.

The loading value was determined for each experimental run and is tabulated above. It can be clearly observed that the loading values are less than 0.5 for every case. It indicates the formation of 1:1 complex by the butyric acid and TOA. The extraction of carboxylic acids by extractant occurs by intermolecular hydrogen bonding or ion exchange of the extractant group with the acid. It has been earlier discussed also that the use of active diluent favours formation of solvates through specific hydrogen bonding between the proton of the diluent and the acid−amine complex. Such ionic interactions often result in formation of 1:1 complex and the fact is reinforced by the value of the loading ratio being less than 0.5 as described by equation (6). The equilibrium complexation constant ($K_{E(1:1)}$) values are evaluated and listed in the tables given above. The unit of $K_{E(1:1)}$ is in $(gmol/lit)^{-1}$. The value of $K_{E(1:1)}$ of 115.89 $(gmol/lit)^{-1}$ has been obtained for extraction of 0.05M butyric acid using 5% TOA in decanol at 40^0C.

The effect of temperature was also studied for the equilibrium experiments. The experiments were conducted for four different temperatures of 25^0C, 30^0C, 35^0C and 40^0C. It can be clearly observed from the tables that both extraction efficiency and distribution coefficient increase with increasing temperature. This can be traced back to the fact that the reactive extraction of butyric acid using TOA in decanol proceeds through formation of acid-amine complex which further form solvates with the diluent. High temperature favours higher degree of dissociation of hydroxyl ion, which renders the proton of the decanol available for formation of solvates.

4.2. Extraction Kinetics

The kinetic study of reactive extraction was performed by taking into account six different initial butyric acid concentrations, using two different TOA concentrations in decanol at four different temperatures. The change in concentration of butyric acid in the organic phase and aqueous phase has been plotted against time at which the concentrations have been evaluated.

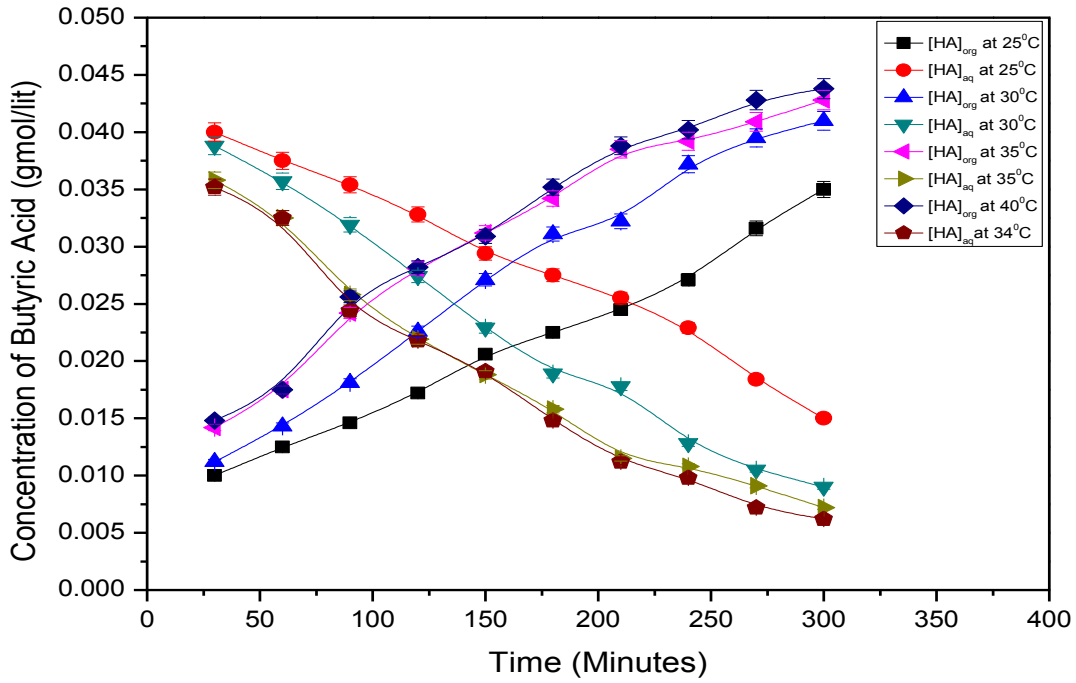

Fig: 4.1- Extraction of 0.05M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.05M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.1×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.2×10^{-3} minute^{-1} at 35^0C and 6.2×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

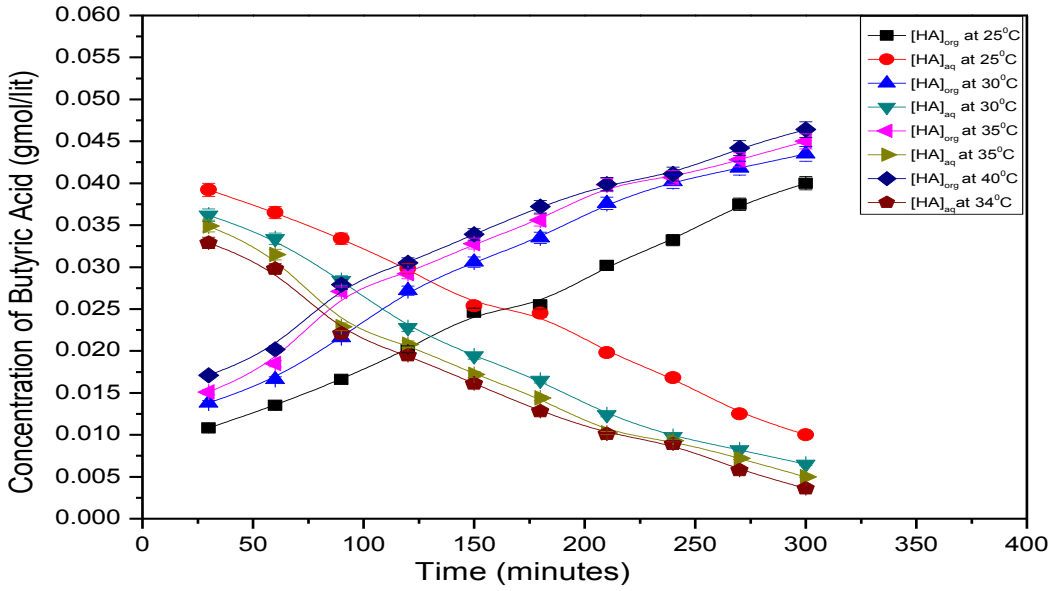

Fig: 4.2- Extraction of 0.05M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.05M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.7×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

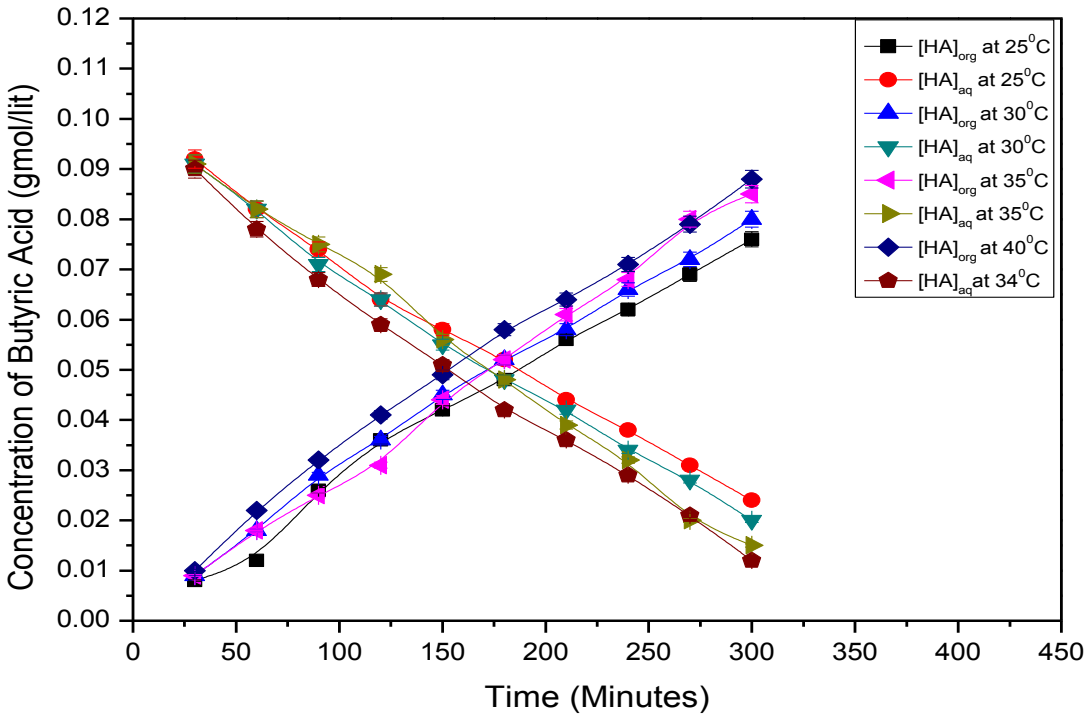

Fig: 4.2.3- Extraction of 0.1M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.1M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 3.9×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.2×10^{-3} minute^{-1} at 35^0C and 6.3×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

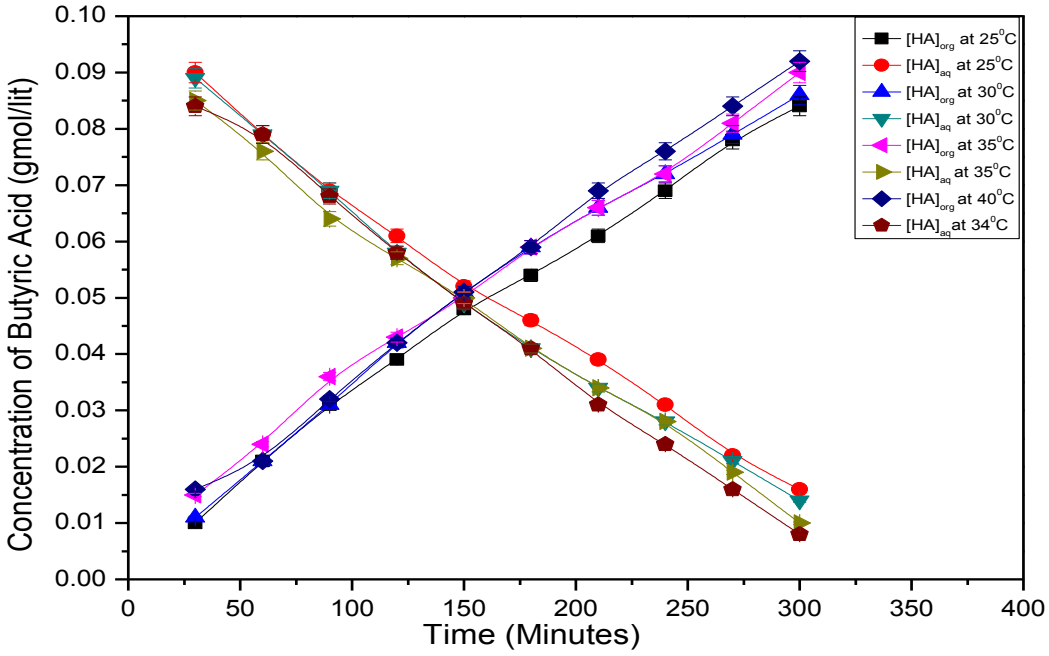

Fig: 4.4- Extraction of 0.1M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.1M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.8×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

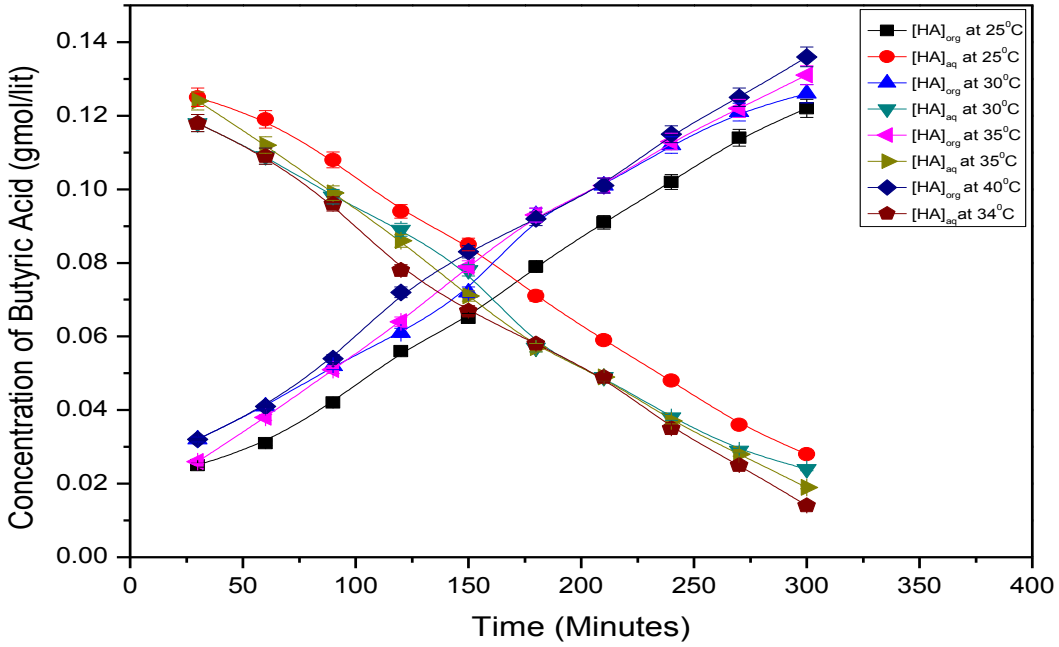

Fig: 4.5- Extraction of 0.15M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.15M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.2×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.21×10^{-3} minute^{-1} at 35^0C and 6.2×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

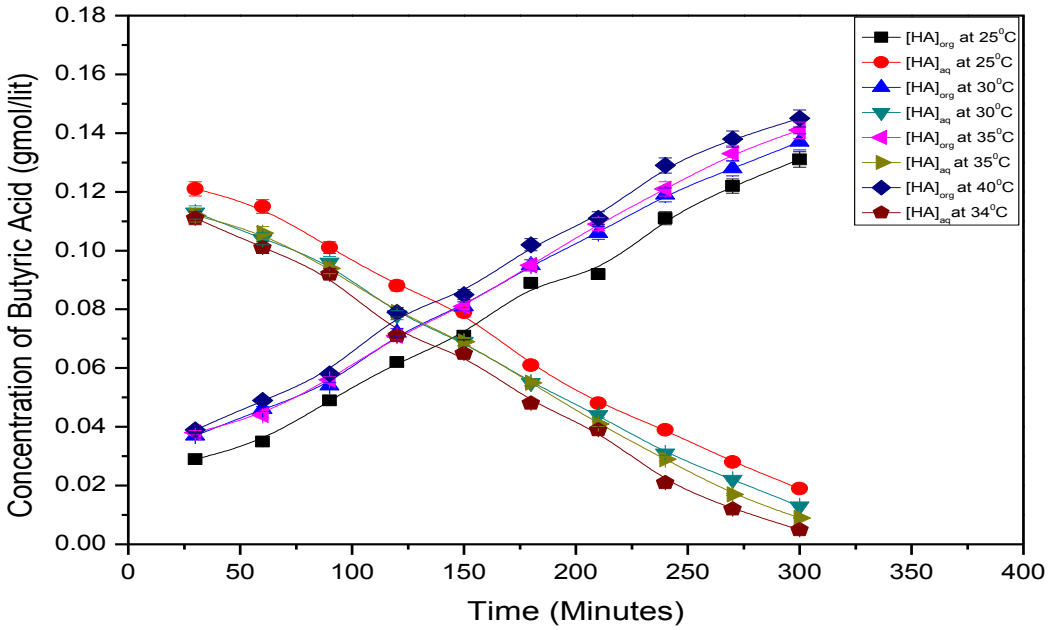

Fig: 4.6- Extraction of 0.15M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.15M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.8×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

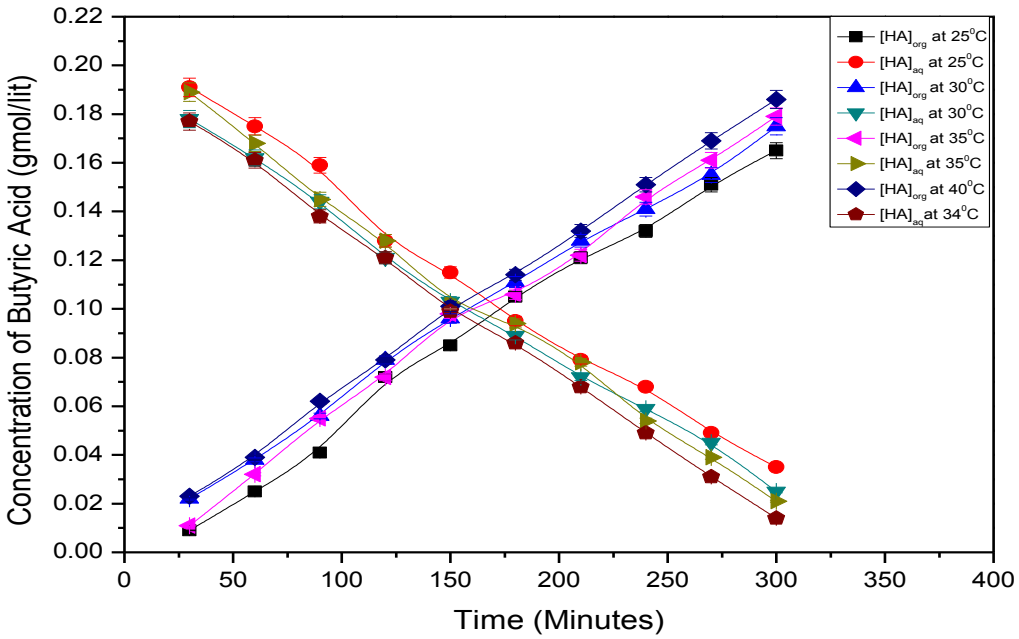

Fig: 4.7- Extraction of 0.2M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.2M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 3.9×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.2×10^{-3} minute^{-1} at 35^0C and 6.2×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

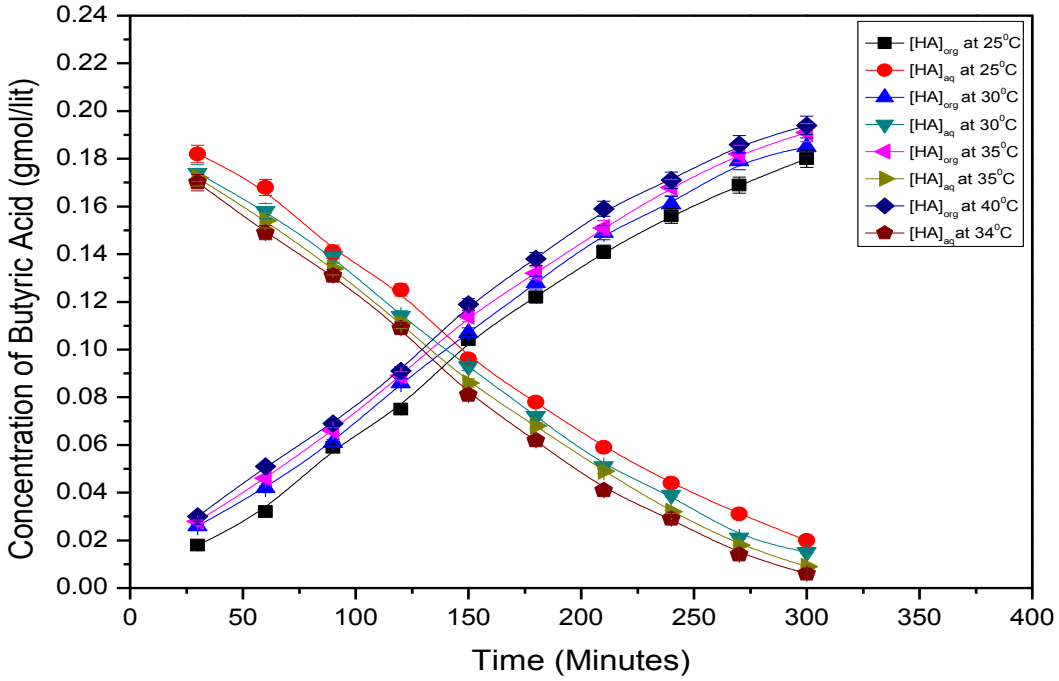

Fig: 4.8- Extraction of 0.2M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.2M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.8×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

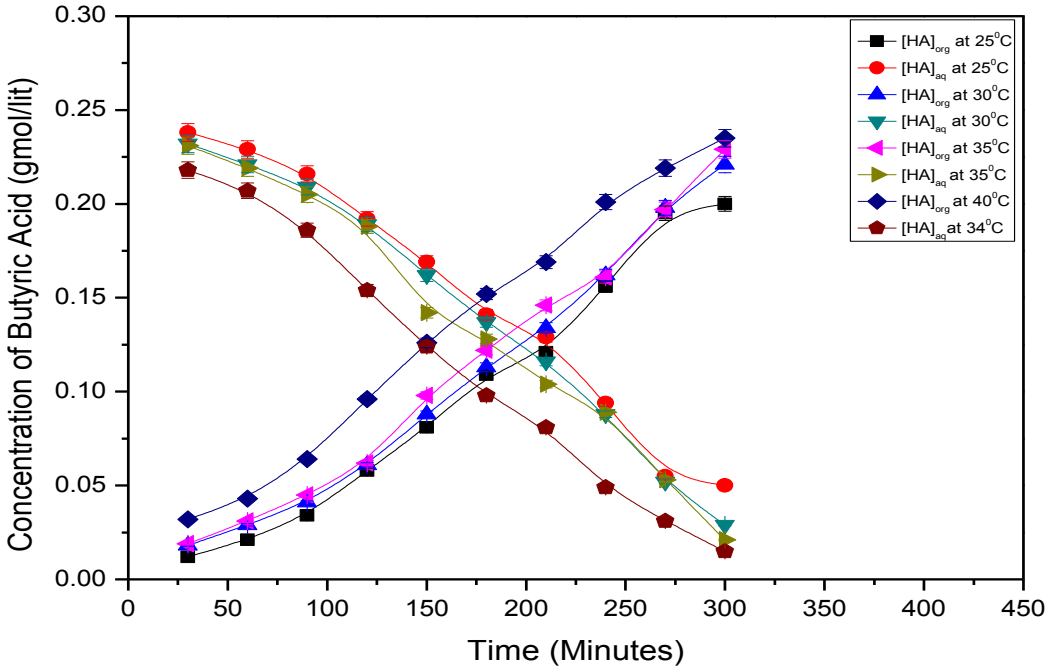

Fig: 4.9- Extraction of 0.25M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.25M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.1×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.2×10^{-3} minute^{-1} at 35^0C and 6.2×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

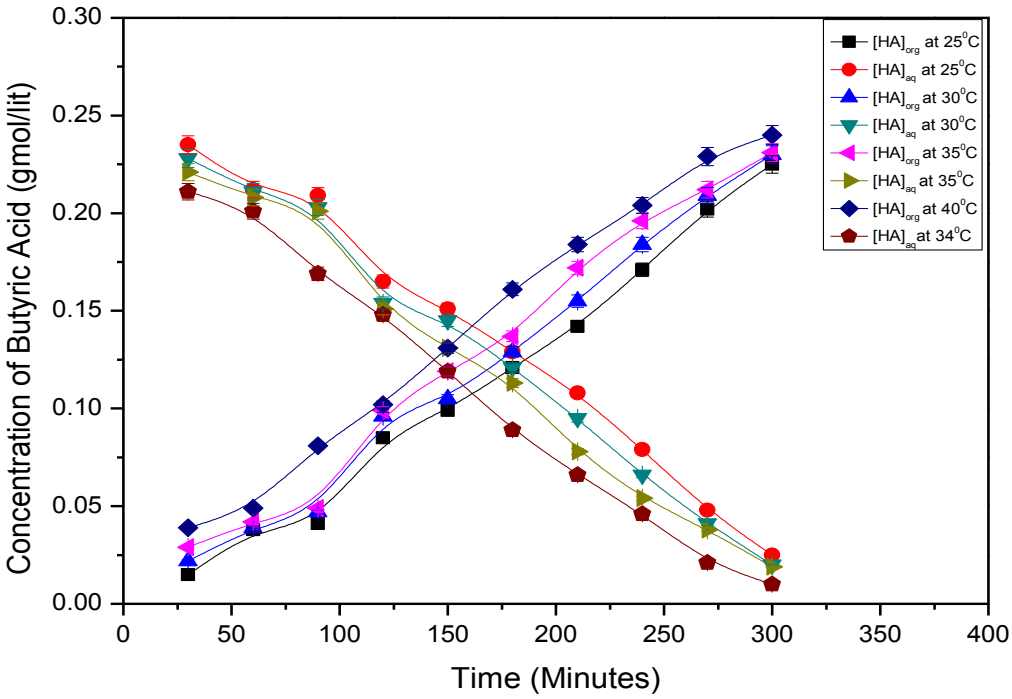

Fig: 4.10-Extraction of 0.25M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.25M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.8×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

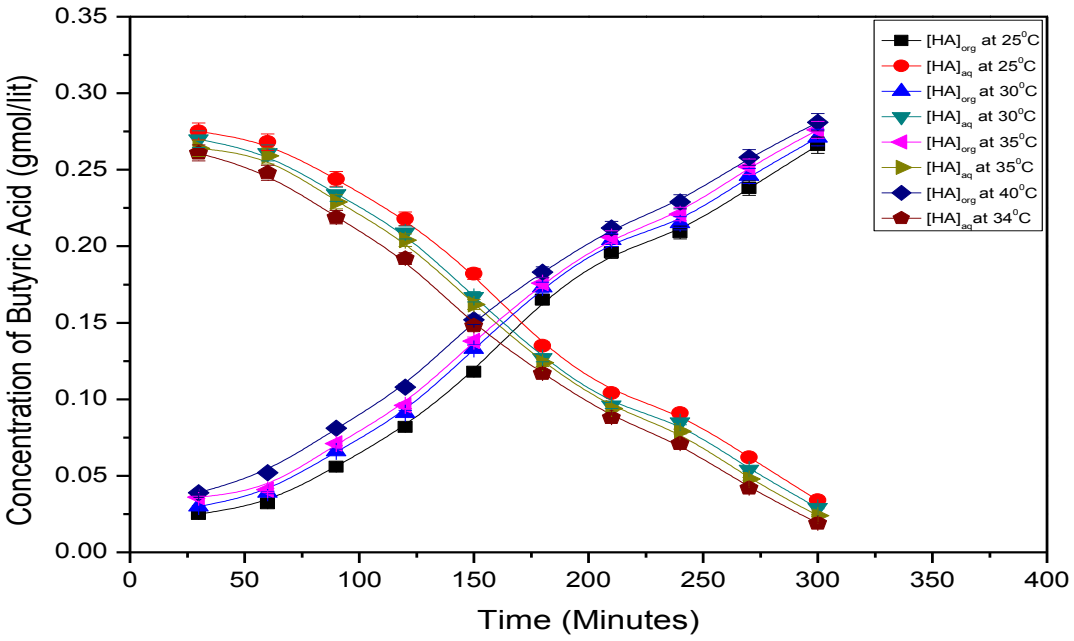

Fig: 4.11- Extraction of 0.3M butyric acid using 5% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.3M butyric acid using 5% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.1×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.2×10^{-3} minute^{-1} at 35^0C and 6.2×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

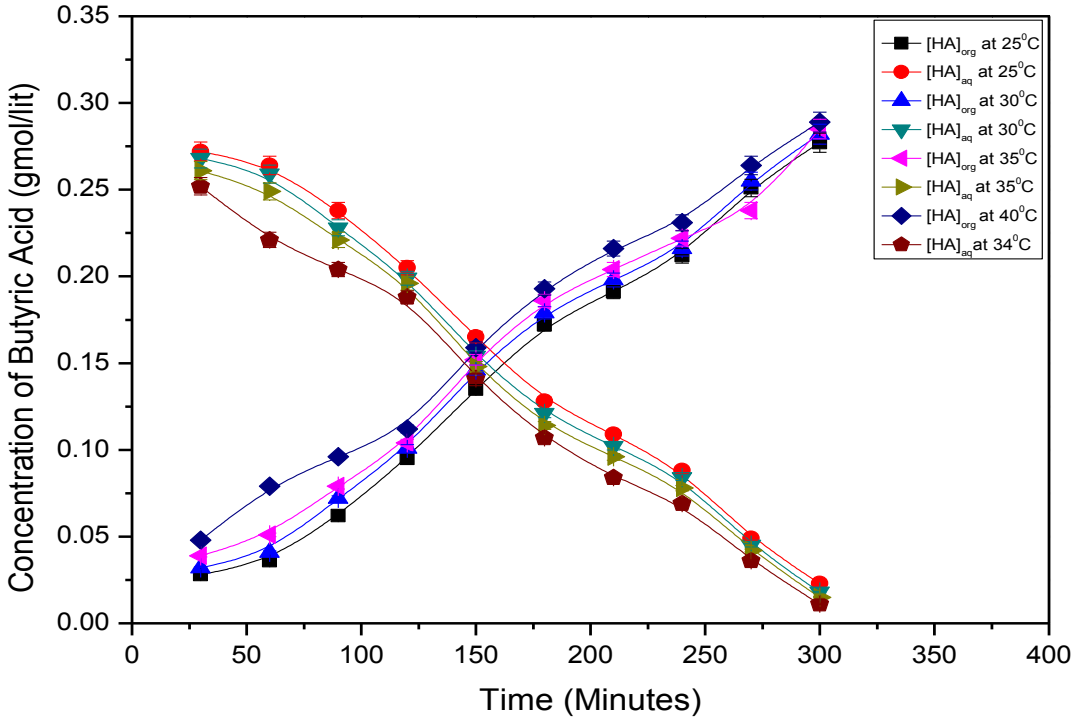

Fig: 4.12- Extraction of 0.3M butyric acid using 10% TOA in decanol

From the above figure it can be observed that the kinetic study of extraction of 0.3M butyric acid using 10% TOA (v/v) in decanol at 25^0C, 30^0C, 35^0C and 40^0C showed a trend similar to that of a first order reaction kinetics. The concentration of the butyric acid in the aqueous phase decreased with time and that in the organic phase increased with time. Also as the temperature increased the rate of extraction increased as is evident from the figure. The rate constants evaluated at different temperatures for the extraction of butyric acids are 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.8×10^{-3} minute^{-1} at 35^0C and 6.9×10^{-3} minute^{-1} at 40^0C. From the rate constant values, it is also evident that the rate increases with time.

From the plots, it can be observed that the concentration of the butyric acid in the organic phase increased with time and that in aqueous phase decreased with time. Also it can be observed that with the increase of temperature the rate of extraction increased. The concentration plot converges earlier for higher temperature and later for lower temperatures.

The value of mass transfer coefficient can be obtained from the following equation (3.8)-

$$V_{aq}\times\frac{dC_{org}}{dt}=K_L\times A_C\times(C^*_{org}-C_{org})$$

On integrating equation-(3.8), we get equation (3.9).

$$K_L = \frac{V_{aq}}{A_c \times t} \int \frac{dC_{org}}{\left(C^*_{org} - C_{org}\right)}$$

Where,

V_{aq}= Volume of aqueous phase. = 100 ml.

A_c= Cross-Sectional area of base of conical flask = 100 cm^2

t = Time of extraction = 300 minutes.

C_{org}= Concentration of butyric acid in organic phase.

C^*_{org}= Equilibrium concentration of butyric acid in organic phase.

The mass transfer coefficient is obtained by evaluating equation-(3.9).

The values of the mass transfer coefficient for different concentrations of butyric acid at different concentrations of TOA in decanol and at different temperatures are listed in the following table. The mass transfer coefficients are expressed in terms of $K_L \times 10^{-3}$ cm/min.

Table: 4.17- Mass transfer coefficients for extraction of butyric acid using TOA in decanol at different temperatures and different TOA concentration in decanol

Initial Concentration of Butyric Acid in gmol/lit	**Mass transfer coefficient, K_L at 25^0C for 5% TOA**	**Mass transfer coefficient, K_L at 25^0C for 10% TOA**	**Mass transfer coefficient, K_L at 30^0C for 5% TOA**	**Mass transfer coefficient, K_L at 30^0C for 10% TOA**	**Mass transfer coefficient, K_L at 35^0C for 5% TOA**	**Mass transfer coefficient, K_L at 35^0C for 10% TOA**	**Mass transfer coefficient, K_L at 40^0C for 5% TOA**	**Mass transfer coefficient, K_L at 40^0C for 10% TOA**
0.05	6.93	9.44	12.45	12.65	13.76	11.45	13.84	12.55
0.10	8.72	10.3	10.15	11.30	11.26	12.76	11.37	11.52
0.15	12.43	11.73	11.61	12.81	11.73	12.91	11.85	12.61
0.20	11.75	12.76	12.61	11.79	12.74	11.89	12.45	12.58

The value of the mass transfer coefficient, K_L lied between 6.93×10^{-3}- 12.91×10^{-3} cm/min. The average value of the mass transfer coefficient, K_L is 10.77×10^{-3} cm/min.

The order of the reactive extraction process was determined by integral method of analysis of the kinetic data and was found to be of first order. The corresponding rate constants were evaluated at different temperatures and are tabulated below. The rate constants are expressed in the table as $(k\times10^{-3})$ $minute^{-1}$.

Table: 4.18- Rate constants for extraction of butyric acid using TOA in decanol at different temperatures and different TOA concentration in decanol

Initial Concentration of Butyric Acid in gmol/lit	Rate Constant, k at 25^0C for 5% TOA	Rate Constant, k at 25^0C for 10% TOA	Rate Constant, k at 30^0C for 5% TOA	Rate Constant, k at 30^0C for 10% TOA	Rate Constant, k at 35^0C for 5% TOA	Rate Constant, k at 35^0C for 10% TOA	Rate Constant, k at 40^0C for 5% TOA	Rate Constant, k at 40^0C for 10% TOA
0.05	4.06	4.50	4.62	4.89	5.22	5.77	6.22	6.92
0.10	3.99	4.52	4.61	4.89	5.19	5.78	6.28	6.92
0.15	4.15	4.48	4.59	4.91	5.21	5.79	6.23	6.95
0.20	3.98	4.46	4.61	4.88	5.23	5.79	6.21	6.97
0.25	4.07	4.50	4.61	4.90	5.17	5.81	6.22	6.89
0.30	4.06	4.51	4.61	4.91	5.22	5.81	6.23	6.91

From the above table it can be clearly observed that the reaction rate constants are increasing with temperature and also with increase in extractant concentration in the organic phase.

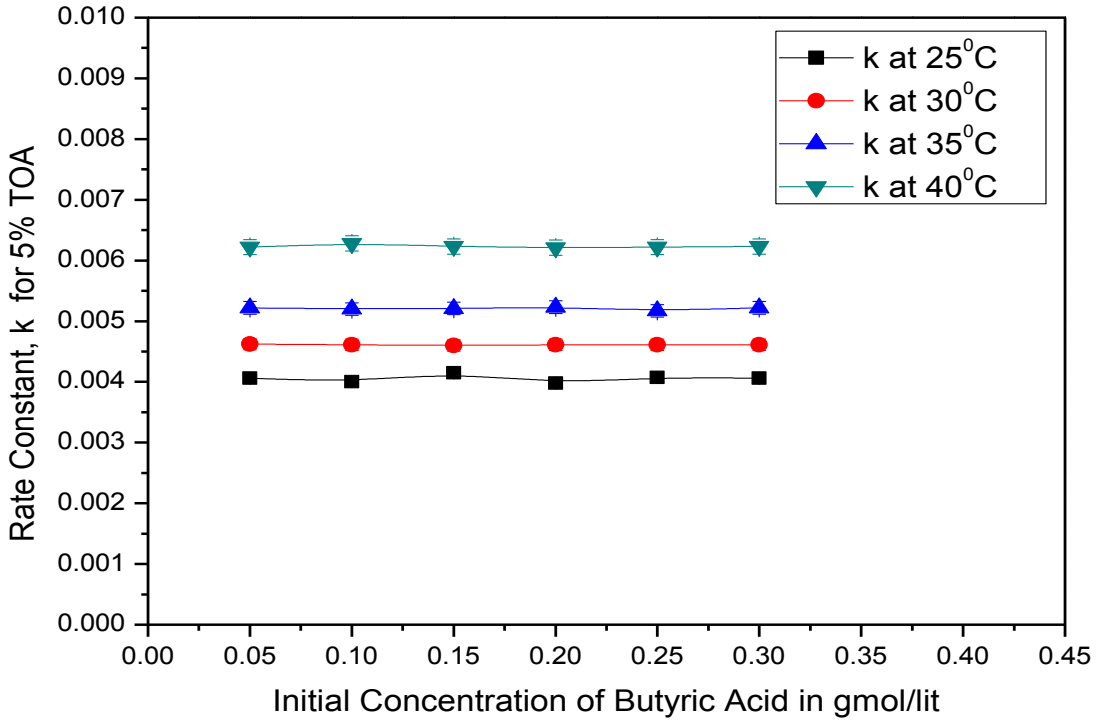

Fig: 4.13- Rate constants of extraction of butyric acid using 5% TOA in decanol

The plot of rate constant versus initial butyric acid concentration for extraction using 5% TOA in decanol at different temperatures yielded straight lines which indicate that the rate

expression satisfied first order kinetics. The rate constant increased with increase in temperature which accords with the Arrhenius theory. The rate constant increased from 3.99×10^{-3} minute^{-1} at 25^0C to 6.28×10^{-3} minute^{-1} at 40^0C.

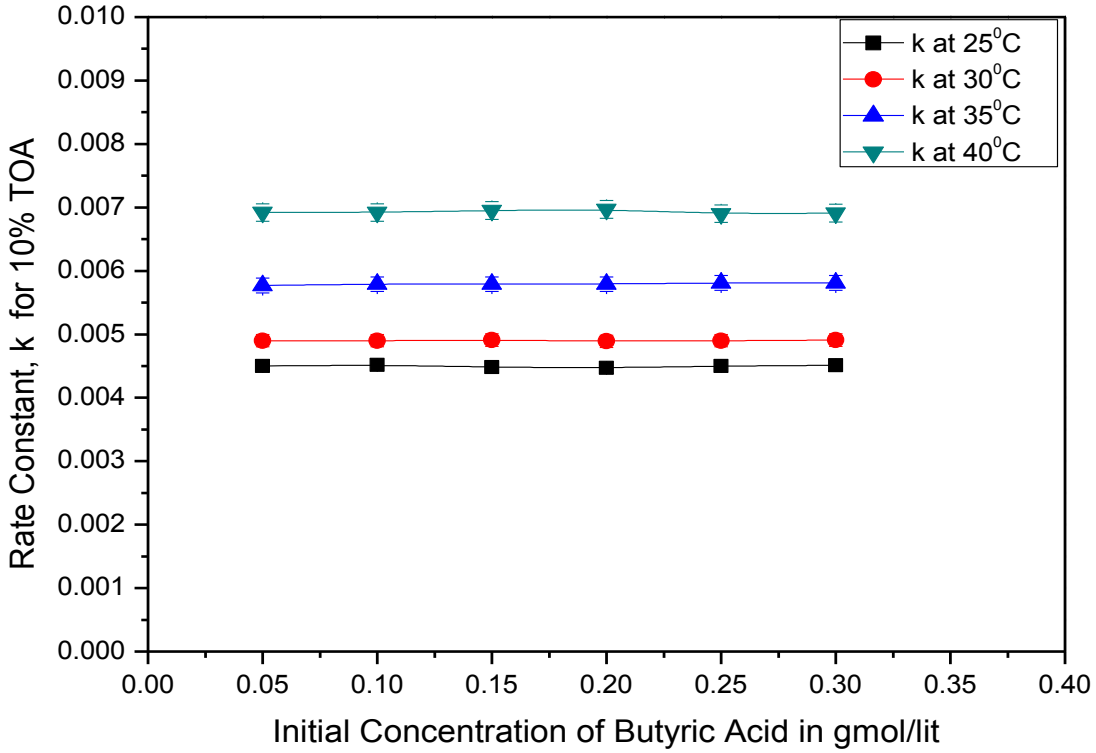

Fig: 4.14- Rate constants of extraction of butyric acid using 10% TOA in decanol

The plot of rate constant versus initial butyric acid concentration for extraction using 10% TOA in decanol at different temperatures yielded straight lines which indicate that the rate expression satisfied first order kinetics. The rate constant increased with increase in temperature which accords with the Arrhenius theory. The rate constant increased from around 4.46×10^{-3} minute^{-1} at 25^0C to 6.97×10^{-3} minute^{-1} at 40^0C.

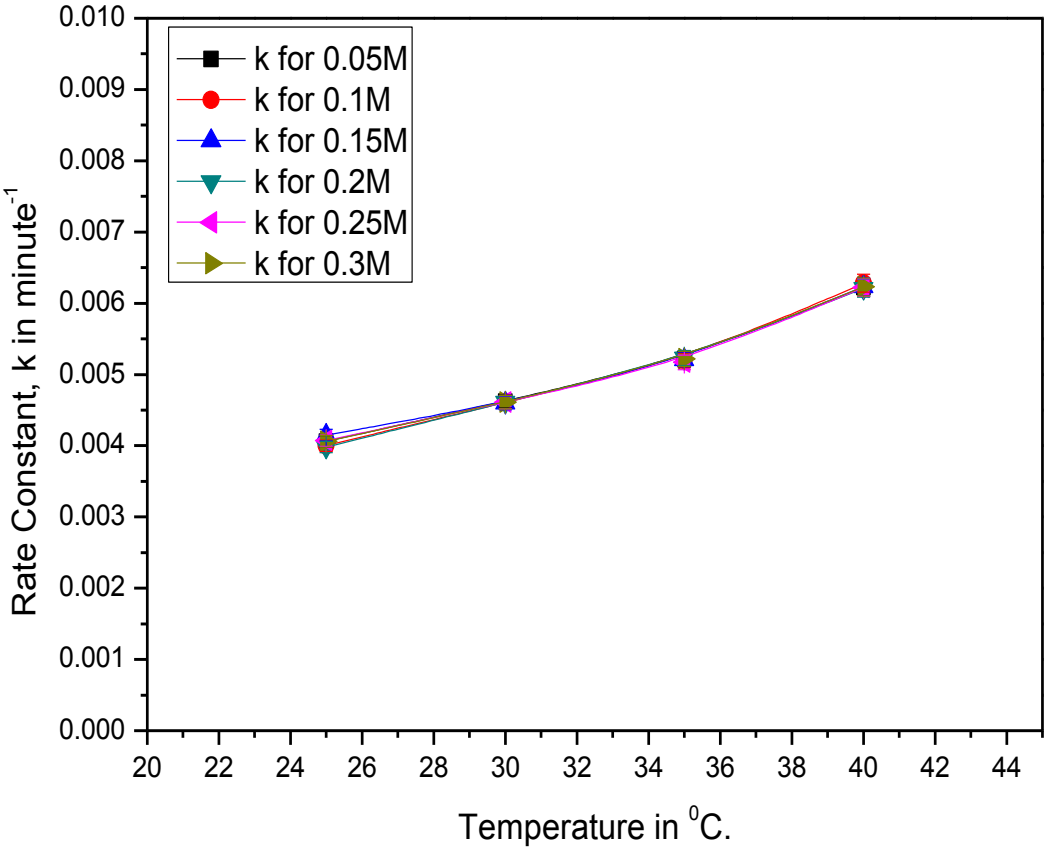

Fig: 4.15- Rate constants for extraction of various concentrations of butyric acid using 5% TOA in decanol

The plot of rate constant versus temperature for extraction of butyric acid using 5% TOA in decanol showed that the rate constant steeply increased with temperature. The rate constant is independent of concentration of butyric acid. The rate constant increased with increase in temperature which accords with the Arrhenius theory. The rate constant increased from 3.99×10^{-3} minute^{-1} at 25^0C to 6.5×10^{-3} minute^{-1} at 40^0C.

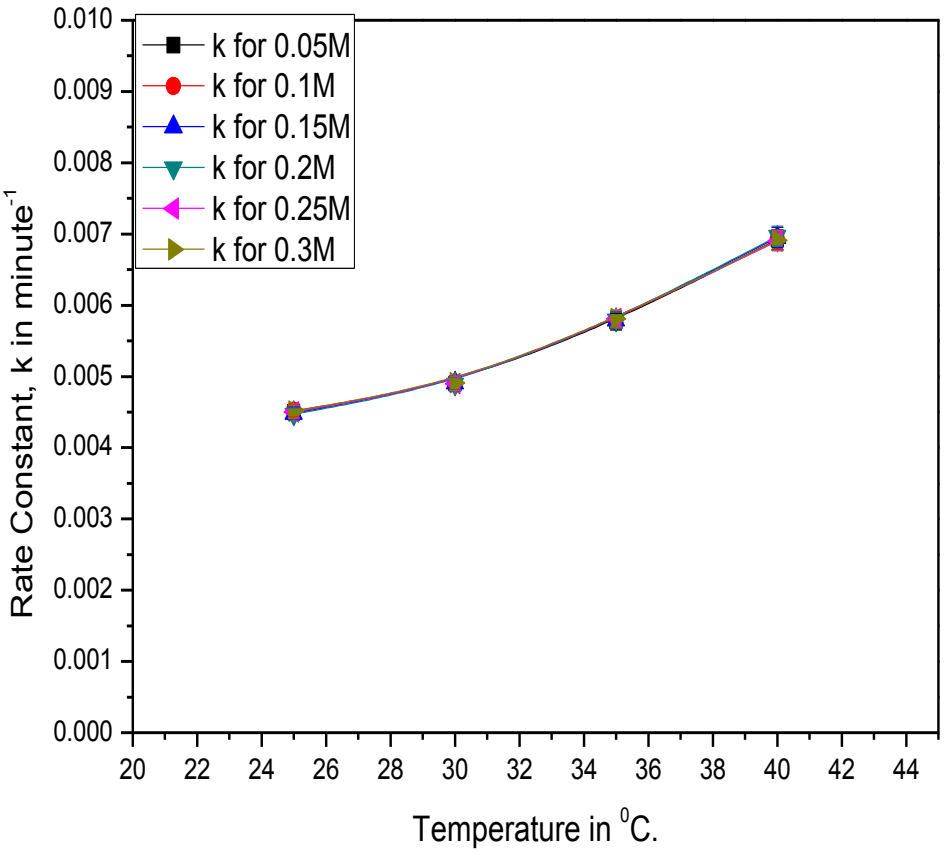

Fig: 4.16- Rate constants for extraction of various concentrations of butyric acid using 10% TOA in decanol

The plot of rate constant versus temperature for extraction of butyric acid using 10% TOA in decanol shows that the rate constant steeply increases with temperature. The rate constant is independent of concentration of butyric acid. The rate constant increases with increase in temperature which accords with the Arrhenius theory. The rate constant increases from around 4.46×10^{-3} minute^{-1} at 25^0C to 6.97×10^{-3} minute^{-1} at 40^0C.

CHAPTER: 5
CONCLUSION

5. Conclusion

The present work of "Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol" deals with two important aspects of reactive extraction modelling. They are the equilibrium study and the kinetic study. The effect of temperature on the extraction process is also very important and has been studied with very high precision.

From the equilibrium study the following conclusions can be drawn.

- For the physical extraction of butyric acid using decanol only, the highest extraction efficiency of 45.5% and the highest distribution coefficient value of about 0.83 was achieved at 40^0C for the extraction of 0.2M aqueous butyric acid solution.
- For the chemical extraction of butyric acid with TOA in decanol, distribution coefficient increased from 4 for extraction of 0.05M butyric acid solution using 5% TOA in decanol at 25^0C, to 49 for 0.3M butyric acid solution using 10% TOA in decanol at 40^0C. Also, the extraction efficiency has improved from 80% for extraction of 0.05M butyric acid solution using 5% TOA in decanol at 25^0C, to 98% for 0.3M butyric acid solution using 10% TOA in decanol at 40^0C.
- The loading values are less than 0.5 for every case. It indicates the formation of 1:1 complex by the butyric acid and TOA. The extraction of carboxylic acids by extractant occurs by intermolecular hydrogen bonding or ion exchange of the extractant group with the acid.
- Both extraction efficiency and distribution coefficient increases with increasing temperature.

From the kinetic study following conclusions can be drawn.

- For extraction of 0.05M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 4.06×10^{-3} minute^{-1} at 25^0C, 4.62×10^{-3} minute^{-1} at 30^0C, 5.22×10^{-3} minute^{-1} at 35^0C and 6.22×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol, the rate constant values were found to be 4.5×10^{-3} minute^{-1} at 25^0C, 4.89×10^{-3} minute^{-1} at 30^0C, 5.77×10^{-3} minute^{-1} at 35^0C and 6.92×10^{-3} minute^{-1} at 40^0C.
- For extraction of 0.1M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 3.99×10^{-3} minute^{-1} at 25^0C, 4.61×10^{-3} minute^{-1} at 30^0C, 5.19×10^{-3} minute^{-1} at 35^0C and 6.27×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol, the

rate constant values were found to be 4.52×10^{-3} minute^{-1} at 25^0C, 4.89×10^{-3} minute^{-1} at 30^0C, 5.78×10^{-3} minute^{-1} at 35^0C and 6.92×10^{-3} minute^{-1} at 40^0C.

- For extraction of 0.15M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 4.15×10^{-3} minute^{-1} at 25^0C, 4.6×10^{-3} minute^{-1} at 30^0C, 5.21×10^{-3} minute^{-1} at 35^0C and 6.23×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol, the rate constant values were found to be 4.48×10^{-3} minute^{-1} at 25^0C, 4.91×10^{-3} minute^{-1} at 30^0C, 5.79×10^{-3} minute^{-1} at 35^0C and 6.95×10^{-3} minute^{-1} at 40^0C.
- For extraction of 0.2M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 3.98×10^{-3} minute^{-1} at 25^0C, 4.61×10^{-3} minute^{-1} at 30^0C, 5.23×10^{-3} minute^{-1} at 35^0C and 6.21×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol, the rate constant values were found to be 4.47×10^{-3} minute^{-1} at 25^0C, 4.89×10^{-3} minute^{-1} at 30^0C, 5.79×10^{-3} minute^{-1} at 35^0C and 6.97×10^{-3} minute^{-1} at 40^0C.
- For extraction of 0.25M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 4.07×10^{-3} minute^{-1} at 25^0C, 4.61×10^{-3} minute^{-1} at 30^0C, 5.17×10^{-3} minute^{-1} at 35^0C and 6.22×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol the rate constant values were found to be 4.5×10^{-3} minute^{-1} at 25^0C, 4.9×10^{-3} minute^{-1} at 30^0C, 5.81×10^{-3} minute^{-1} at 35^0C and 6.89×10^{-3} minute^{-1} at 40^0C.
- For extraction of 0.3M butyric acid using 5% TOA (v/v) in decanol, the rate constant values were found to be 4.06×10^{-3} minute^{-1} at 25^0C, 4.61×10^{-3} minute^{-1} at 30^0C, 5.22×10^{-3} minute^{-1} at 35^0C and 6.23×10^{-3} minute^{-1} at 40^0C. By using 10% TOA (v/v) in decanol, the rate constant values were found to be 4.51×10^{-3} minute^{-1} at 25^0C, 4.91×10^{-3} minute^{-1} at 30^0C, 5.81×10^{-3} minute^{-1} at 35^0C and 6.91×10^{-3} minute^{-1} at 40^0C.
- The value of the mass transfer coefficient, K_L lied between 6.93×10^{-3}- 12.91×10^{-3} cm/min. The average value of the mass transfer coefficient, K_L was found to be 10.77×10^{-3}cm/min.
- The order of the kinetics of the reactive extraction process is found to be of first order.
- The reaction rate constants increase with temperature and also with increase in extractant concentration in the organic phase. The rate constant increased from 3.99×10^{-3} minute^{-1} at 25^0C to 6.5×10^{-3} minute^{-1} at 40^0C using 5% TOA in decanol and from 4.6×10^{-3} minute^{-1} at 25^0C to 6.97×10^{-3} minute^{-1} using 10% TOA in decanol at 40^0C.

CHAPTER: 6
FUTURE SCOPE

6. Future Scope

The present work on "Reactive Extraction of Butyric Acid using Tri-Octyl Amine in Decanol" deals with two important aspects of reactive extraction modelling. They are the equilibrium study and the kinetic study. However some scopes have remained which needs further attention.

The process of reactive extraction deals with mixing of chemicals of different pH values and hence the pH has a strong effect on the rate and degree of extraction. Maintenance of lower pH always favours reaction involving weak acids such as acetic acid, propionic acid, etc. However, under certain pH condition the extractant does not effectively form complex with the acid and hence lower degree of extraction is achieved.

Also, pH influences the kinetics of the extraction process and alters it with its changing values.

Hence, it is very important to study the effect of pH on the reactive extraction process for the particular acid-extractant-diluent system.

Here, active diluent have been used for the study. One can also opt for inactive diluents like toluene and determine the various parameters of reactive extraction.

CHAPTER: 7
REFERENCES

7. References

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